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(54) NEAR INFRARED ABSORBING TRANSPARENT RESIN COMPOSITION AND ITS MOLDING

(57)Abstract:

PURPOSE: To obtain a composition, industrially useful as an optical filter, a heat ray absorbing glazing material, etc., due to its manifestation of excellent near infrared absorptivity without causing the instability such as fading and the photochromism such as fading by allowing thereof to stand in the dark for a long period.

CONSTITUTION: The characteristic of this near infrared ray absorbing transparent resin composition comprises thermally kneading 100 pts.wt. transparent resin with 0.01-5 pts.wt. cupric sulfide having 0.05-4 μ m average particle diameter. Furthermore, this near infrared absorbing transparent resin molding is obtained by molding the composition into a sheetlike or a filmlike shape. Since the near infrared absorbing sheet thus obtained has a strong absorptivity over the whole near infrared region of 800-2000nm wavelength, the sheet can be utilized as an optical material such as a near infrared cutting filter, a recording material, a heat ray screening material, a thermal storage material, a near infrared detecting sensor, etc.

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CLAIMS

[Claim(s)]

[Claim 1] (A) Transparence resin It is (B) to the 100 weight sections. Transparence resin constituent excellent in the near infrared ray absorbing power which comes to blend the second copper 0.01 with a mean particle diameter of 0.05-4 micrometers of sulfuration - 5 weight sections.

[Claim 2] The near infrared ray absorption transparence resin Plastic solid with which it comes to fabricate the transparence resin constituent excellent in near infrared ray absorbing power according to claim 1 a sheet and in the shape of a film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the charge of a near infrared ray absorber. Researches and developments are the functional material currently performed briskly, and especially the charge of a near infrared ray absorber can be used recently as optical materials, such as information record ingredients, such as sensitive material which makes the light source semiconductor laser light which has the wavelength of a near infrared region, and a record ingredient for optical disks, an infrared cut filter, and a film, and a heat ray absorptivity grading ingredient.

[0002]

[Description of the Prior Art] As conventionally shown in a U.S. Pat. No. 3692688 specification as a light transmission nature ingredient of near infrared ray absorptivity, they are tungsten hexachloride (WCl_6) and tin chloride ($SnCl_2 \cdot 2H_2O$). The ingredient excellent in the near infrared ray absorbing power which dissolves in methyl-methacrylate syrup (monomer) and is acquired by carrying out a polymerization and which does not have Hayes substantially is known.

[0003] Furthermore, in addition to this as a charge of a near infrared ray absorber developed until now, it is [JP,60-42269,B] in an anthraquinone derivative and JP,61-218551,A to a thiol nickel complex and JP,61-115958,A in chromium, cobalt complex salt, and JP,60-21294,B. 700-800nm The new squarylium compound which has absorption maximum wavelength in a field is indicated.

[0004]

[Problem(s) to be Solved by the Invention] the conventional charge of a near infrared ray absorber had the trouble that as for the thing of an organic system endurance be bad and early capacity deteriorated in connection with change and the passage of time of an environmental condition, and on the other hand, although the thing of a complex system be durable, it had the problem that there be much what not only the near-infrared section but a visible region have absorption, and the compound itself be color strongly, and an application will be restrict. Furthermore, on the wavelength as which the absorption peak was regarded in specific wavelength and both of the things of a system shifted [wavelength] from the peak, it was what absorbing power does not almost have. If the record object which makes the light source laser light which has the wavelength of the near-infrared section is considered using these materials, it is necessary to double the wavelength of laser, and the absorption peak of an ingredient. However, the combination with which also in the wavelength of laser the wavelength of laser and the absorption peak of the charge of a near infrared ray absorber agree since only that to which the absorption wavelength of the charge of a near-infrared absorber was also restricted is obtained could not but become a ***** thing.

[0005] Moreover, WCl_6 of the above-mentioned conventional technique Although it had the property which the constituent which dissolved $SnCl_2 \cdot 2H_2O$ in methyl-methacrylate syrup colors in dark blue, and absorbs a near infrared ray well, it had the trouble of carrying out tenebrescence between prolonged neglect in a dark place. Thus, the photochromism which advances gently was a trouble which is not desirable when offering the industrial products equipped with fixed quality, such as a light filter and heat ray absorptivity grading.

[0006]

[Means for Solving the Problem] When this invention person etc. made the second copper of sulfuration of a specific particle size contain in transparence resin as a result of repeating examination wholeheartedly, absorption was seen uniformly in the 800-2000nm whole near infrared region, and coloring completed header this invention for the charge

of a near infrared ray absorber in which endurance was excellent few being obtained.

[0007] That is, this invention is (A). Transparence resin It is (B) to the 100 weight sections. It is related with the transparence resin constituent excellent in the near infrared ray absorbing power which comes to blend the second copper 0.01 with a mean particle diameter of 0.05-4 micrometers of sulfuration - 5 weight sections. Moreover, this invention offers the near infrared ray absorption transparence resin Plastic solid with which it comes to fabricate the transparence resin constituent excellent in such near infrared ray absorbing power a sheet and in the shape of a film.

[0008] As transparence resin used in this invention, although polycarbonate system resin, styrene resin, methacrylic ester system resin, vinyl chloride system resin, polyolefine system resin, polyester system resin, polyamide system resin, unsaturated polyester system resin, etc. can be mentioned, it is not limited to these.

[0009] With polycarbonate system resin, make dihydric phenol and a carbonate precursor react with a solution method or scorification, and it is manufactured. If the typical example of dihydric phenol is given 2 and 2-screw (4-hydroxyphenyl) propane [bisphenol A], Screw (4-hydroxyphenyl) methane, 1, and 1-screw (4-hydroxyphenyl) cyclohexane, 2 and 2-screw (4-hydroxy - 3, 5-dimethylphenyl) propane, 2, and 2-screw (4-hydroxy - 3, 5-methylphenyl) propane, screw (4-hydroxyphenyl) sulfide, a screw (4-hydroxyphenyl) sulfone, etc. are mentioned. Desirable dihydric phenol uses a screw (4-hydroxyphenyl) alkane system, especially bisphenol A as the main raw material. Moreover, as a carbonate precursor, carbonyl halide, carbonyl ester, or halo formate is mentioned, and they are specifically the dihaloformate and such mixture of a phosgene, diphenyl carbonate, and dihydric phenol.

[0010] A kind of monomer chosen as a styrene monomer list from each group which consists of this monomer and other vinyl monomers which can be copolymerized with styrene resin is used at least. Furthermore, if needed, also make the rubberlike substance exist and it is obtained. A styrene monomer is what names generically styrene, alpha methyl styrene, the styrene derivative with which the hydrogen atom of a benzene nucleus was permuted by the alkyl group of a halogen atom or carbon numbers 1-2. If a thing typical as this styrene monomer is illustrated, they will be styrene, o-KURORU styrene, p-methyl styrene, 2, 4-dimethyl styrene, or t-butyl styrene. moreover, to a thing typical as other above mentioned vinyl monomers which can be copolymerized Acrylonitrile, alpha-chloro acrylonitrile, or the acrylonitrile system monomer like cyanidation vinylidene; (meta) An acrylic acid, (Meta) A methyl acrylate, an ethyl acrylate (meta), butyl acrylate (meta), (Meta) The acrylic acids like metaglycidyl acrylate, acrylic-acid (meta)-2-ethylhexyl butyl, or (meta) acrylic-acid-beta-hydroxyethyl (meta) and those various ester acid; or vinyl acetate, (Meta) A vinyl chloride, a vinylidene chloride, vinyl pyrrolidone, acrylamide (meta), a maleic anhydride, itaconic acid anhydride, or maleimide is begun, and there is vinyl ketones or vinyl ether. Furthermore, in a thing typical as the above mentioned rubberlike substance, it is conjugation like isoprenes including polybutadiene rubber, styrene butadiene styrene block copolymerization rubber, ethylene-propylene terpolymer system rubber, butadiene acrylonitrile copolymerization rubber, isobutylene isoprene rubber, acrylic rubber, styrene isobutylene butadiene copolymerization rubber, or isoprene acrylic ester system copolymerization rubber, or a chloroprene. Although there is rubber obtained using 1 and 3-diene system monomer, these are used in a kind or two sorts or more of combination.

[0011] It is manufactured by the polymerization nature partial saturation monomer which uses a methyl methacrylate or a methyl methacrylate as a principal component as a polymerization nature raw material, and methacrylic ester system resin is an acrylic acid (meta) (mind of an acrylic acid or a methacrylic acid.) as an example of a methyl methacrylate and the polymerization nature partial saturation monomer which can be copolymerized. Like the following, a methyl acrylate, an ethyl acrylate (meta), acrylic-acid (meta) propyl, Butyl acrylate, acrylic-acid (meta) cyclohexyl, 2-ethylhexyl acrylate (meta), (Meta) Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, trimethylolethane tri(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, neopentyl GURIKORUJI (meta) acrylate, an acrylic-acid (meta) allyl compound, acrylic-acid (meta) hydroxyethyl, etc. can mention as an example. When using the polymerization nature partial saturation monomer which uses a methyl methacrylate as a principal component as a polymerization raw material, it is desirable to include a methyl methacrylate 60% of the weight or more preferably 50% of the weight or more. It is desirable for the method of obtaining a partial polymerization object by massive precuring or the approach of dissolving a polymerization object in a monomer to be mentioned as an approach of obtaining the syrup which contains the polymer of this monomer in the polymerization nature partial saturation monomer which uses a methyl methacrylate or a methyl methacrylate as a principal component as a polymerization raw material, as usually carried out, and to adjust to 35 or less % of the weight of polymer content in consideration of the impregnation at the time of casting. Moreover, the methacrylic ester system resin manufactured using the suspension polymerization which

are the following typical polymerization methods, an emulsion polymerization, and solution polymerization can also be used.

[0012] Although gay vinyl chloride resin excellent in thermal stability, tensile strength, and thermal resistance is desirable as vinyl chloride system resin, little **** blend polymer does not interfere further the vinyl chloride system copolymer which makes a subject the vinyl chloride to which copolymerization of a small amount of comonomer was carried out, a graft copolymer, vinyl chloride system resin and resin with sufficient compatibility, for example, a vinylidene chloride, an ethylene-vinylacetate copolymer, chlorinated polyethylene, etc., either. Furthermore, such mixture is also useful.

[0013] Polyolefine system resin is the homopolymer of an alpha olefin, and a copolymer with the different-species monomer which uses an alpha olefin as a principal component, for example, polyethylene, polypropylene, ethylene propylene rubber, an ethylene-butene copolymer, an ethylene-4-methyl-1-pentene copolymer, an ethylene-vinylacetate copolymer, an ethylene-acrylic-acid copolymer, etc. are mentioned. A consistency among these 0.910-0.935 30 or less % of the weight of an ethylene-vinylacetate copolymer has low density polyethylene, an ethylene-alpha olefin copolymer, and a desirable vinyl acetate content as a film for agriculture from the point of transparency, weatherability, or a price. Furthermore, 5 % of the weight or more and 30% of the weight or less of an ethylene-vinylacetate copolymer has a more desirable vinyl acetate content in respect of transparency, flexibility, weatherability, etc. also among these.

[0014] As polyamide system resin and polyester system resin, nylon 6, Nylon 66, Nylon 12, Nylon 46, polyethylene terephthalate, polybutylene terephthalate, polyacrylate, a polyether ether ketone, etc. can be illustrated.

[0015] the second copper of sulfuration used for this invention -- mean particle diameter -- 0.05-4 micrometers it is -- desirable -- 0.05-3 micrometers it is . As a pulverizing method, a Henschel mixer is used, the second copper of sulfuration is added to polycarbonate resin, and they are a rotational frequency 1500 - 3000rpm. By mixing for 5 - 10 minutes The interior of a room is made into the high-speed turning room of air in the approach and multi-number compression Ayr which carry out pulverization to homogeneity, and small quantity every, although the jet mill approach of making it pulverizing by the collision of the second copper of sulfuration and wall surface collision by adding is suitable, these approaches do not limit the second copper of sulfuration there. Mean particle diameter is 0.05 micrometers. When it is the following, a particle causes secondary condensation and distribution worsens, and it is 4 micrometers. If mixed shaping of the resin is carried out as it is when exceeding, the crystal of the second copper of sulfuration itself will remain in a sheet, and it is 20-100. mum It becomes a big foreign matter and the number is also 10-100 numbers per two 1m. It results in the numerousness of individuals and let mold goods be a defective. Moreover, 4 micrometers When exceeding, it is a near infrared ray. (heat ray) Penetrating well, the effectiveness becomes low.

[0016] the addition of the second copper of sulfuration -- transparence resin the 100 weight sections -- receiving -- 0.01 - 5 weight section -- it is 0.02 - 3 weight section preferably. When the addition of the second copper of sulfuration is under the 0.01 weight section, improvement in near infrared ray absorbing power is not enough, and when the addition of the second copper of sulfuration exceeds 5 weight sections on the other hand, the improvement in near infrared ray absorbing power is not found, but has a possibility that Hayes may occur in an ingredient. Moreover, also with the same content, when the resin ingredient obtained at this invention is a plate, since permeability changes with the board thickness, finally it can determine a content as the appearance from which the permeability in the set-up board thickness is obtained.

[0017] It sets to this invention and is the following general formula (I) further because of improvement in an absorption effect and transparency. One or more sorts of amide derivatives chosen in the compound expressed with one or more sorts of the thiourea derivatives and/or the following general formulas (II) which are chosen from the compounds expressed can be used.

[0018]

[Formula 1]



[0019] [(R1, R2, and R3 may express among a formula the monad chosen from the group which consists of heterocycle residue of hydrogen, an alkyl group, a cycloalkyl radical, an aryl group, an aralkyl radical, 5 members, or 6 members,

each radical may have one or more substituents, R1, R2, or R2 and R3 may connect, and they may form a ring.) 0020]

[Formula 2]



[0021] the inside of a formula, and R4 and R5 -- hydrogen, an alkyl group, an alkenyl radical, and a cycloalkyl radical - the monad chosen from the group which consists of heterocycle residue of an aryl group, an aralkyl radical, 5 members, or 6 members may be expressed, or R5 may express an alkoxy group, each radical may have one or more substituents, and R4 and R5 may connect and they may form a ring. General formula used by this invention (I) Although the following can be illustrated as a thiourea derivative shown, it is not limited to these.

[0022] 1-ethyl-3-phenyl thiourea, 1, 3-diphenyl thiourea, 1, 3-diethyl thiourea, 1-ethyl-3-p-chlorophenyl thiourea, 1-ethyl-3-(2-hydroxyethyl) thiourea, 1-(2-thiazolyl)-3-phenyl thiourea, 1 and 3-distearyl thiourea, 1, 3-dibehenyl thiourea, 1-ethyl thiourea, 1-p-BUROMO phenyl-3-phenyl thiourea, 1-(2-thiophenyl)-3-phenyl thiourea, 1, 3-screw (2-hydroxyethyl) thiourea, 1-p-aminophenyl-3-phenyl thiourea, 1-p-nitrophenyl-3-phenyl thiourea, 1-p-hydroxyphenyl-3-phenyl thiourea, 1, 3-G m-KURORU phenyl thiourea, Ethylene thiourea, thiourea, 1-methyl-3-p-hydroxyphenyl thiourea, 1-phenyl thiourea, 1-m-nitrophenyl thiourea, 1-p-nitrophenyl thiourea, 1-p-aminophenyl thiourea, 1, 3-dimethyl thiourea, 1, 3-dicyclohexyl thiourea, 1-phenyl-3-p-chlorophenyl thiourea, 1-phenyl-3-p-methoxyphenyl thiourea, 1, and 1-diphenyl thiourea, 1, and 1-dibenzyl-3-phenethyl thiourea, 1-phenyl-3-(2-hydroxyethyl) thiourea.

[0023] Although the following can be illustrated as an amide derivative shown by the general formula (II) used by this invention, it is not limited to these.

[0024] N-methyl Benz amide, N-phenyl Benz amide, and N-phenyl stearyl amide, A N-ethyl ethyl amide and an N-ethyl-p-KURORU Benz amide, A N-propyl Benz amide, N-ethyl stearyl amide, and an N-1-(2 thiazolyl) Benz amide, A N-stearyl stearyl amide and N-behenyl behenyl amide, An acetamide, an N-phenyl-p-BUROMO Benz amide, and N-behenyl acetamide, A N-p-aminophenyl Benz amide and an N-p-nitrophenyl Benz amide, A N-p-hydroxyphenyl Benz amide and an N-m-KURORU phenyl Benz amide, Nicotinamide, an acetanilide, O-ethyl-N-phenyl (carbamate), The Benz amide, m-nitro Benz amide, p-nitro Benz amide, p-amino Benz amide, N-methyl acetamide, N-cyclohexyl Benz amide, N-chlorophenyl Benz amide, a N-p-methoxyphenyl Benz amide, and N-stearyl Benz amide.

[0025] the addition of a thiourea derivative and/or an amide derivative -- transparency resin the 100 weight sections -- receiving -- 0.001 - 1 weight section -- desirable -- 0.002-0.5 It is the weight section. The addition of a thiourea derivative and/or an amide derivative When there is no addition effectiveness in being under the 0.001 weight sections, and the addition of a thiourea derivative and/or an amide derivative exceeds 1 weight section on the other hand, although an absorption effect is remarkable, its fall of transparency is also remarkable.

[0026] In addition, reinforcing materials, such as a suitable additive also with effective and also adding and using dispersants, such as a sorbitan fatty acid ester like sorbitan monostearate and a glycerine fatty acid ester like glycerol monostearate, to the constituent of this invention, in order to make more distribution of the second copper of sulfuration other than the above-mentioned component into fitness if needed, for example, a flame retarder, a thermostabilizer, an anti-oxidant, light stabilizer, an ultraviolet ray absorbent, lubricant, a coloring agent, an inorganic bulking agent, and a glass fiber, etc. can also be blended.

[0027] It can manufacture easily with the mixed equipment, for example, the hot calender roll, Banbury mixer, or extruder of common use, without requiring a special means and sequence as the mixed approach of the transparency resin in this invention, the second copper of sulfuration, a thiourea derivative, and/or an amide derivative.

[0028] A film or a sheet is easy to be manufactured according to the usual manufacturing method. It can manufacture by the T-die method by the extruder, the inflation-molding method, the calender fabricating method, and compression forming.

[0029] Although there is especially no limit, as for the thickness of a film or a sheet, it is desirable that it is within the limits of 0.01-10mm. In addition, when increasing the reinforcement of a sheet further or attaching a pattern, the interior is made to contain the glass fiber network and the wire gauze made from stainless steel which knit and wove glass filament yarn in the shape of [of about 5mm angle] a grid, and they may be fabricated.

[0030]

[Function] like the above -- mean particle diameter -- 0.05-4 micrometers Carry out heating kneading by the above-

mentioned mixed approach at the transparence resin containing the second copper of sulfuration. the 800-2000nm whole region -- crossing -- about -- although it comes to absorb a near infrared ray to Mr. one, the detailed mechanism of action is not yet clear.

[0031]

[Example] Although an example is hung up over below and detail of this invention is given, this invention is not limited to these. In addition, all the addition rates in the following examples show the weight section.

[0032] Moreover, the transparency spectrum of the obtained resin ingredient was measured with the spectrophotometer (Hitachi Make: 323 mold).

[0033] The judgment of near infrared ray absorbing power is 900, 1300, and a near infrared ray absorption value with a wavelength [each] of 1600 or 1900nm. (%) It expressed.

[0034] Mean diameter pulverized by the example 1 jet-mill approach 1.6 micrometers Polycarbonate resin which consists the second copper of sulfuration of bisphenol A As opposed to the 100 weight sections 0.1 weight sections addition is carried out, and it mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 300 degrees C. Subsequently, this pellet is dried, an injection molding machine is used, and it is thickness. The green transparence resin plate without 0.7mm Hayes was created. A transparency spectrum is measured about these obtained plates, and the result is shown in Table 1.

[0035] Example of comparison 1 mean diameter 9.5 micrometers Polycarbonate resin which consists the second copper of sulfuration of bisphenol A As opposed to the 100 weight sections 0.1 weight sections addition is carried out, and it mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 220 degrees C. Subsequently, this pellet is dried, an injection molding machine is used, and it is thickness. The green transparence resin plate without 0.7mm Hayes was created. A transparency spectrum is measured about these obtained plates, and the result is shown in Table 1.

[0036] An injection molding machine is used for the polycarbonate resin which consists of second copper [of example of comparison 2 sulfuration] additive-free bisphenol A, and it is thickness. The transparence resin plate without 0.7mm Hayes was created. A transparency spectrum is measured about these obtained plates, and the result is shown in Table 1.

[0037]

[Table 1]

	近赤外線吸収性 (%)			
	900nm	1300nm	1600nm	1900nm
実施例 1	65	74	75	77
比較例 1	57	68	64	65
比較例 2	28	23	23	32

[0038] According to Table 1, it is mean particle diameter. 1.6 micrometers It is clear the sheet's of the transparence resin which kneaded the second copper of sulfuration to become a strong near infrared ray absorptivity sheet.

[0039]

[Effect of the Invention] As stated above, this invention Transparence resin It is the mean particle diameter of 0.05-4 micrometers to the 100 weight sections. Since it is the near infrared ray absorption transparence resin Plastic solid which it comes to fabricate the shape of a near infrared ray absorption transparence resin constituent and a sheet, or a film characterized by carrying out heating kneading of the second copper 0.01 of sulfuration - the 5 weight sections Since there is no instability, such as tenebrescence, and the photochromism of carrying out tenebrescence to a dark place by prolonged neglect is not seen, either but the obtained resin ingredient shows the outstanding near infrared ray absorbing power, it is industrially useful as optical filter and heat ray absorptivity grading material etc.

[0040] Moreover, obtained near infrared ray absorption sheet It has the strong absorptivity covering the 800-2000nm near infrared region whole region. It can use by using these properties as optical materials, such as a near infrared ray cut-off filter, a record ingredient, a heat ray shielding material, a **** ingredient, a near infrared ray detection sensor, etc.

[Translation done.]